

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF SLURRIES

(71) We, INTERNATIONAL DRILLING FLUIDS (U.K.) LTD., a British Company, of 8, St. Bride Street, London, EC4A 4DA, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of slurries of water-soluble salts, especially of salts which are to be used in very humid or marine environments such as on drilling rigs at sea. As used herein, the term "water-soluble" implies that a saturated solution of the salt can be prepared from a salt/water mixture containing less than 72% by weight of dry solid salt.

Large quantities of water-soluble salts, for example potassium chloride, are used in preparing drilling muds. Conventionally the salts are supplied to a drilling rig in solid form in bags. However in highly humid conditions most water-soluble salts will absorb water and will tend to form hard cakes in the bag which are very difficult to handle and dissolve. This problem is particularly serious with potassium chloride which, at 80% relative humidity, absorbs 1% of its own weight of water in 24 hours. Also, since the salt is generally required to be used in aqueous solution, it would render it unnecessary to provide special heavy duty mixing equipment for dissolving the solid salt and would ease the problem of handling bags of solid material in restricted space and frequently in adverse weather conditions if the salt could be provided in solution or in suspension in water.

It is known to provide water-soluble salts, such as potassium chloride, for use on marine drilling rigs in the form of an aqueous solution, but at 15°C. the solubility of potassium chloride is 32.4 g per 100 g of water or 11.3 pounds per barrel of water (1 barrel=35 imperial gallons), and therefore even if the salt is supplied as a saturated solution—and usually the concentration will be a little less than the saturation concentration—a large amount of water must be transported with the

salt and this increases the transportation costs undesirably.

Embodiments of the invention may provide a water-soluble salt in a fluid and easily pumpable form which contains a relatively small proportion of water and is stable over a period of a month or more in that the viscosity remains substantially constant and little if any solid material is deposited on the bottom of the container for the salt.

According to the present invention there is provided a method of preparing an aqueous slurry of a water-soluble salt, which method comprises:

- (i) preparing an aqueous solution or colloidal dispersion of a water-soluble or -dispersible viscosity-increasing polymer, and
- (ii) incorporating into the solution or dispersion of the polymer from 300 to 900 lb of the water-soluble salt per barrel of said solution or dispersion (i.e. sufficient salt to form a slurry containing from about 46 to about 72% by weight of dry solid salt).

In step (i) the viscosity-increasing polymer may be, for example, a high molecular weight, water-soluble carbohydrate such as a cellulose derivative, a xanthan gum biopolymer, a kayara gum, a guar gum or a swollen starch, or an alkali metal or ammonium polyacrylate of number average molecular weight greater than about 100,000, or a water-soluble alginate. Examples of suitable cellulose derivatives are sodium carboxymethyl cellulose, methyl cellulose, ethyl hydroxy cellulose, ethyl hydroxyethyl cellulose or hydroxypropyl cellulose. Xanthan gum biopolymers are polysaccharides produced by fermentation of a carbohydrate nutrient medium with certain xanthomonas micro-organisms.

Generally, the water-soluble salt will be added to the polymer solution or dispersion in the dry form. It may be possible in at least certain instances to add the water-soluble salt in two stages, firstly as a saturated aqueous solution and next as dry salt. This can be done, for example, where the polymer is xanthan

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gum biopolymer. When using a xanthan gum polymer, it is also possible to use a modification of the procedure defined above, in which a solution of the water-soluble salt is first prepared and the xanthan gum biopolymer added thereto followed by a further quantity of the salt so as to produce a slurry containing *in toto* from 300 to 900 lb of the said salt.

The quantity of polymer used will generally be such as to provide a solution having a concentration in the range from about 0.2 to about 2.0 g of polymer per 100 ml. of solution (i.e. from about 0.7 to about 7.0 lb. per barrel).

The apparatus used for dissolving or dispersing the polymer preferably comprises a tank provided with a rotating propellor, or turbine, type impeller the diameter of which can advantageously be at least equal to one half of the width or diameter of the tank. The tank may be provided with vertical baffles which extend from the walls for substantially their complete height in order to prevent or inhibit the formation of a vortex in the tank during the mixing operation. The number of baffles is conveniently in the range from three to six and the width of the baffles may be, for example, about one tenth of the width or diameter of the tank.

It is advantageous for the pH of the slurry to have an alkaline value, preferably at least 9, since this reduces the corrosiveness of the slurry. The pH can be controlled by the addition of suitable reagents, e.g. sodium carbonate or sodium hydroxide, during the mixing step. It is also advantageous to minimise the entrainment of air during operation of the method.

In step (ii) the water-soluble salt is preferably of small particle size and should consist, for example, of particles substantially all of which have a diameter smaller than 2 mm. If desired the water-soluble salt may be ground into the aqueous solution of polymer in a ball mill. However provided that the particles of the salt are substantially all smaller than 2 mm it is generally more convenient to use apparatus of the type preferred for performing step (i) for mixing the salt with the polymer solution. As a general rule, the finer the salt the less of the viscosifying polymer is required to bring the viscosity of the suspension to the point at which sedimentation of the larger particles does not occur. Advantageously substantially all of the particles of the water-soluble salt have a diameter smaller than 0.5 mm.

During incorporation of the salt into the polymer solution or dispersion, it is advantageous to dissipate at least 3 horsepower hours of energy per ton of dry salt. It is preferable for from 4 to 10 horsepower hours of energy per ton of dry salt to be dissipated.

The method of the invention is most useful for providing concentrated slurries of

chlorides of sodium, potassium or calcium for use on drilling rigs at sea. The salts may be transported to the drilling rig in tanks or barrels and may be metered into the mixing equipment used for forming the drilling mud in the liquid state. This avoids the need for manual handling of bags of solid material and completely eliminates waste of energy and material through the formation in the bags of large cakes of material which are difficult to break up and dissolve.

Slurries prepared in accordance with the invention are most conveniently pumped by means of positive displacement pumps, for example of the diaphragm, piston or peristaltic type. Centrifugal pumps are not generally suitable for the purpose.

The invention is illustrated by the following Examples.

EXAMPLE 1

A concentrated slurry of potassium chloride was prepared in the following manner:

Five litres of water at 10.9°C. were run into mixing equipment comprising a cylindrical tank of diameter 25 cm provided with a six-bladed radial flow turbine impeller of overall diameter 18 cm and for vertical baffles of width 2.5 cm which were spaced equally round the walls. The impeller was started at a speed of 225 rpm and 30.2 g of a xanthan gum biopolymer were added, i.e. sufficient to form a solution of concentration 0.6 g of polymer per 100 ml of solution or 2.1 pounds per barrel. After 25 minutes the polymer was completely dissolved and the speed of the impeller was increased to 311 rpm to compensate for the increase in viscosity of the solution. The total amount of potassium chloride to be added was 11.67 Kg, i.e. sufficient to form a suspension containing 70% by weight of total solids (suspended and dissolved) or 816 pounds of potassium chloride per barrel of water. One half of this quantity of potassium chloride was added in 2 minutes and addition of potassium chloride was then halted for 2 minutes to allow a saturated solution to form with a consequent reduction in the viscosity of the liquid. The remainder of the potassium chloride was added in the space of a further 28 minutes, during which time the speed of the impeller was increased to 460 rpm. The dispersion of the potassium chloride was considered to be complete in a further 5 minutes. The energy dissipated in forming the suspension was 5.9 horsepower hours per ton of dry potassium chloride. The potassium chloride used in this example was in the form of granules having diameters in the range from 1 to 2 mm. The resultant slurry had a viscosity of 9.0 poise as measured by a Brookfield Viscometer with a No. 3 spindle at a spindle speed of 100 rpm and was found to be easily pumpable using a compressed air actuated diaphragm pump.

EXAMPLE 2

Two further slurries of potassium chlorides were prepared according to the procedure described in Example 1 and using the same quantity of xanthan gum biopolymer but different quantities of potassium chloride. In each case the viscosity of the final slurry was measured with a Brookfield Viscometer with a No. 3 spindle at 100 rpm and the results are set forth in Table 1 below. The result from Example 1 is included to show more completely the relationship between the concentration of potassium chloride and the viscosity.

TABLE I

Concentration of potassium chloride		
(% by weight of total solids)	(pounds per barrel of water)	Viscosity (poise)
50	350	5.0
60	525	6.5
70	816	9.0

All three slurries were pumpable and little, if any, sedimentation of potassium chloride was observed on storage.

EXAMPLE 3

A further concentrated slurry of potassium chloride was prepared by first mixing 63 g of sodium carboxymethyl cellulose with 7 litres of water to form a solution containing 0.9 g of sodium carboxymethyl cellulose for 100 ml of water or 3.1 pounds per barrel. The apparatus described in Example 1 was used and solution of the sodium carboxymethyl cellulose was complete in 105 minutes. 7 Kg of potassium chloride in the form of granules of diameters in the range 1—2 mm were then added to the solution and the mixture transferred to a ball mill of diameter 18 inches and length 18 inches and filled to 70% of its volume with pebbles of diameters in the range 1—2 inches. The mill was run for 30 minutes and at the end of this time a homogeneous, pumpable slurry containing 50% by weight of potassium chloride (350 pounds per barrel of water) was formed. The energy dissipated in forming the slurry was 5 horsepower hours per ton of dry potassium chloride.

EXAMPLE 4

A concentrated slurry of potassium chloride was prepared using apparatus as shown in the accompanying drawing. The apparatus consists of a tank 1 having a conical bottom section and provided with a propeller type mixer 2 driven by a 3 h.p. electric motor 3. To the lowest part of the conical bottom of the tank there is connected an outlet conduit 4 through which the contents of the tank may be drawn by means of a centrifugal pump 5 which is driven by a 20 HP electric motor at 1460 rpm. The delivery of the pump is connected to a conduit 6 which can communicate either with

a conduit 7 leading to a container for storing or transporting the slurry, or with a conduit 8 which returns the slurry to the tank 1. Conduit 7 is closed by a valve 9 and conduit 8 by a valve 10. It is important that the lowest part 11 of the conduit 8 should be below the level 12 of liquid in the tank in order to minimise entrainment of air in the slurry which would render the slurry more corrosive. The viscosity-increasing polymer is supplied to the tank 1 in dry form by a hopper 13, the water-soluble salt is supplied in dry form by a hopper 14 and water by a conduit 15. Tank 1, as shown in the drawing, was filled with 210 gallons of water and sufficient sodium hydroxide was added with stirring to raise the pH to 10.0. 50 lb of dry potassium chloride was then added from the hopper 14 and dissolved in the water with stirring. There was then added from hopper 13 15 lb of the same xanthan gum biopolymer as was used in Example 1, i.e. sufficient to form a solution of concentration 0.7 g of polymer per 100 ml of solution or 2.5 pounds per barrel, and the suspension was agitated by means of mixer 2 and by recirculating the contents of the tank through pump 5 and conduit 8 for 2 hours in order to disperse the polymer fully and allow it to develop its full viscosifying properties. With the pump and mixer still in operation, sufficient potassium chloride was then added to increase the concentration of the salt to 460 lb of potassium chloride per barrel of water or 57% by weight of dry solid salt.

The total energy dissipated during the mixing operation was about 5 hp-hr of energy per ton of dry potassium chloride. The rheological properties of the final suspension were determined with a Fann VG Viscometer, which is a rotational viscometer which measures the shear stress on a cylindrical bob, restrained by a torsion spring, the shear stress being transmitted by the fluid in the annular space between the bob and a rotating coaxial cylinder. The shear stress is measured at different shear rates by changing the speed of rotation of the rotating cylinder. In order to obtain the apparent viscosity, plastic viscosity and yield point, measurements of shear stress are made at shear rates of 1022 sec⁻¹, which corresponds to a rotational speed of 600 r.p.m., and 511 sec⁻¹, which corresponds to a rotational speed of 300 r.p.m. The dial of the instrument is calibrated directly in centipoise.

The apparent viscosity is given by $\frac{1}{2}$ (dial reading at 600 rpm); plastic viscosity by (dial reading at 600 rpm—dial reading at 300 rpm); and the yield point by (dial reading at 300 rpm—Plastic viscosity). In order to determine the gel strength the sample is stirred vigorously with a high speed stirrer which is then switched off. After the desired test time (10 sec. or 10 min.) the rotating cylinder is rotated at 3 rpm and the maximum deflec-

tion shown on the dial before the gel breaks is recorded. The gel strength is a measure of the structure which builds up when the fluid is under low shear conditions and gives an indication of the suspending properties of the fluid.

The following results were obtained.

Apparent viscosity (centipoise)	62
Plastic viscosity (centipoise)	31
Yield point (lb/100 ft ²)	62
Gel strength after 10 sec. (lb/100ft ²)	17
Gel strength after 10 min. (lb/100 ft ²)	21

The slurry was stored for 8 weeks and after this time there was no appreciable increase in viscosity and no sedimentation of the salt; the slurry was still readily pumpable.

WHAT WE CLAIM IS:—

1. A method of preparing an aqueous slurry of a water-soluble salt, which method comprises:

(i) preparing an aqueous solution or colloidal dispersion of a water-soluble or -dispersible viscosity-increasing polymer, and

(ii) incorporating into the solution or dispersion of the polymer from 300 to 900 lb of the water-soluble salt per barrel of said solution or dispersion (i.e. sufficient salt to form a slurry containing from about 46 to about 72% by weight of dry solid salt).

2. A method according to claim 1, in which a high molecular weight, water-soluble carbohydrate is used as said polymer.

3. A method according to claim 2, wherein the carbohydrate is cellulose or a derivative thereof.

4. A method according to claim 1, wherein there is used a xanthan gum biopolymer as said polymer.

5. A modification of the method according to claim 1, in which a solution of the water-soluble salt is first prepared and the xanthan gum biopolymer added thereto followed by a further quantity of the salt so as to produce a slurry containing *in toto* from 300 to 900 lb of the said salt.

6. A method according to claim 1, wherein there is used, as said polymer, a kayara gum, a guar gum or a swollen starch.

7. A method according to claim 1, wherein there is used an alkali metal or ammonium polyacrylate of number average molecular weight greater than about 100,000 as said polymer.

8. A method according to claim 1, wherein

a water-soluble alginate is used as said polymer.

9. A method according to claim 3, wherein there is used one of sodium carboxymethyl cellulose, methyl cellulose, ethyl hydroxy cellulose, ethyl hydroxyethyl cellulose and hydroxypropyl cellulose.

10. A method according to any preceding claim, wherein the amount of said polymer used is such as to produce a solution or dispersion having a concentration in the range of from 0.2 to 2.0 grams of polymer per 100 ml of solution.

11. A method according to any preceding claim, wherein said water-soluble salt consists of particles substantially all of which have a diameter smaller than 2 mm.

12. A method according to claim 11, wherein substantially all of the particles have a diameter smaller than 0.5 mm.

13. A method according to any one of claims 1 to 4 or 6 to 9, wherein said water-soluble salt is added to the polymer solution in the dry form.

14. A method according to any one of claims 1 to 4 or 6 to 9, wherein the water-soluble salt is added to the polymer solution or dispersion in two stages, firstly as a saturated aqueous solution and secondly as dry salt.

15. A method according to any one of claims 1 to 4, 6 to 9, 13 and 14, wherein there is dissipated, during the incorporation of the water-soluble salt into said polymer solution or dispersion, at least 3 horsepower hours of energy per ton of dry salt.

16. A method according to claim 15, wherein there is dissipated from 4 to 10 horsepower hours of energy per ton of dry salt.

17. A method according to claim 1 or 5 of preparing an aqueous slurry of a water-soluble salt, substantially as described in any one of the foregoing examples.

18. An aqueous slurry of a water-soluble salt whenever produced by a method as claimed in any preceding claim.

19. A drilling mud including an aqueous slurry as claimed in claim 18.

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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

